PFAS in urban stormwater runoff of industrial catchments

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Highlights

- PFAS and other persistent substances found in industrial urban stormwater runoff
- PFOA-equivalent concentrations for PFAS-24 exceeded EU proposal for surface- and groundwater
- Urban stormwater runoff from industrial sites is one source of PFAS in surface waters

Introduction

Per- and polyfluoroalkyl substances (PFAS) have emerged as a significant environmental concern. As a class of synthetic organic compounds that are characterized by their strong carbon-fluorine bonds, the majority of PFAS are highly resistant to degradation in the environment. Due to their favourable properties for many purposes, they have been widely used in industrial processes, firefighting foams, and consumer products, leading to their pervasive presence in urban settings (e.g. Liu et al. 2023). Due to their toxicity, regulations of allowable PFAS concentrations in surface, ground and drinking waters are getting more strict with proposed thresholds in low ng/L range. Understanding of sources and pathways is therefore becoming more important to be able to prevent or mitigate contamination.

Urban stormwater runoff is one potential pathway for the transport of PFAS from various sources to receiving water bodies. Rain water coming in contact with potentially contaminated surfaces and resulting in runoff from impervious urban infrastructure can mobilize and carry these persistent chemicals into storm sewers and eventually into receiving rivers and lakes. The implications of PFAS in stormwater runoff extend beyond mere contamination, posing a potential threat to aquatic ecosystems and also public health, if receiving surface waters are used as drinking water resources (directly or via bank filtration).

Although previous monitoring programs also included single PFAS compounds (mostly PFOS and PFOA), knowledge on sources and pathways is still insufficient, especially in regard to other PFAS compounds with high toxicity that are included in new regulations (e.g. PFNA, PFDA, PFHxS). Nevertheless, new investigations can build on previous findings. In our previous investigation of urban stormwater runoff from different urban catchment types and its contamination with micropollutants, we detected PFOA at concentrations up to 70 ng/L (Wicke et al. 2021). The most frequent detections and the highest concentrations were found in runoff from an industrial catchment, whereas findings in other catchment types (e.g. typical dense residential areas, single family houses, traffic areas) were less frequent and at lower concentrations. Therefore, stormwater runoff from industrial catchments is of special interest in regard to sources of PFAS in urban runoff.

As concerns regarding PFAS and other industrial, persistent, mobile, and toxic substances (iPMTs) intensify, further interdisciplinary research becomes essential to understand contamination pathways and develop effective management practices to safeguard urban water quality. In light of this, monitoring studies are required to provide valuable data but are especially challenging when addressing stormwater runoff, due to their dynamics.

Methodology

In the present study we focused on event-based sampling of stormwater runoff from two adjacent urban catchments with a very high share (94%) of small and medium industrial and commercial areas in the city of Berlin, Germany. The catchment sizes were 36 ha (site GEW) and 6 ha (site MIR). Both catchments included industrial companies which could potentially use PFAS in their processes (e.g. pharmaceuticals, plastic production, metal industry, dry cleaning). In both of the two monitoring catchments, one flow meter

(PCM4, Nivus, Germany) was installed in the storm sewer and one portable automatic sampler (Sigma SD 900, Hach Lange, Germany) was fixed under the storm sewer manhole using suspension harnesses (Figure 1). Each sampler was equipped with a set of 8 × 2 L glass bottles and PE-LD (low density polyethylene) inflow pipes to avoid potential sorption and sample contamination. Established protocols for sampling water samples for PFAS analysis were followed (e.g. EGLE 2018). Automatic samplers were triggered by a pre-assigned water level threshold, varying between 7 and 12 cm. For each storm event to be analysed, a volume-proportional composite sample was prepared based on runoff measurements (for details see Wicke et al. 2021) to allow event mean concentrations to be determined. During 8 months of monitoring (March 2023 to October 2023), a total of 38 volume-proportional composite samples were taken at both monitoring sites (19 each). Stormwater runoff samples were analysed for 109 parameters, including standard parameters (total suspended solids, DOC, and total phosphorous), 26 PFAS, 39 pesticides, 16 PAH and 25 industrial chemicals (4 organophosphates, 3 azoles and 18 volatile organic compounds) in an accredited laboratory in accordance with German standards (DIN).

Figure 1. Left: In-sewer installation of sampler tubing and flow sensor; middle: autosampler in position (photographed from below inside the manhole; photo insert: autosampler suspension harnesses for fixation); right: autosampler installation in a manhole.

Results and discussion

An overview of the concentration ranges of the investigated compound groups is shown in Figure 2 (sum of concentrations of all compounds within one group). Whereas the sum of PFAS ranges between 5 and 35 ng/L, the other groups were present at a higher range with a median concentration of about 0.5 µg/L (except for volatiles/VHCs). The maximum concentration of 27 µg/L occurred for the sum of PAH for a storm event in June 2023 after a long dry period of about seven weeks. From the group of volatile organic compounds (VHCs), only one compound (dioxane) was occasionally detected (13 out of 38 samples, maximum concentration 70 ng/L).

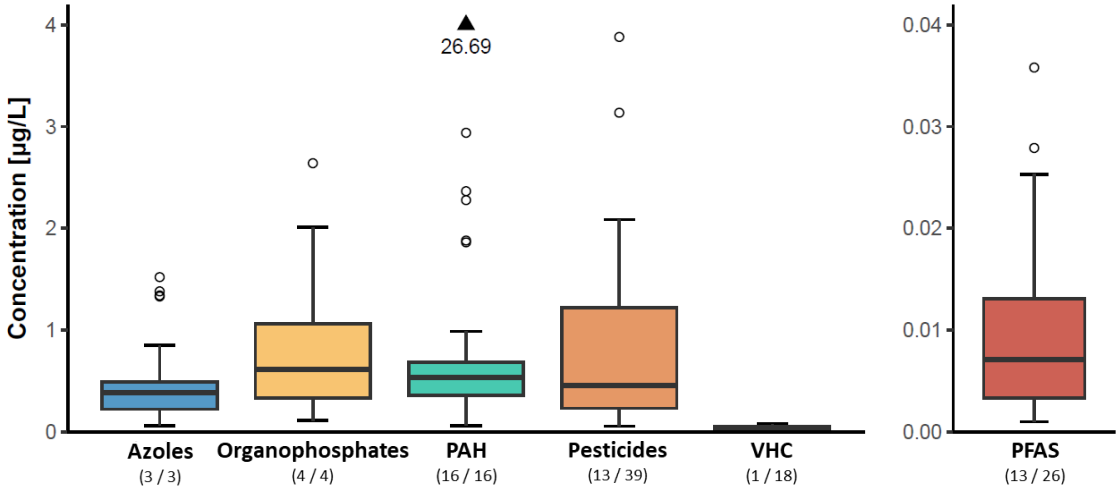

Figure 2. Overview of concentration ranges for the different analysed compound groups as box-whisker plots (horizontal bars – median values, boxes – 25% & 75% quantiles, whiskers – 10% & 90% quantiles, circles – values outside the 10%-90% range). Each group shows the concentration sum for all compounds with values >LOQ within the respective group for all sampled storm events at both sites (n=38). In brackets: number of compounds >LOQ / total number of compounds in each group.

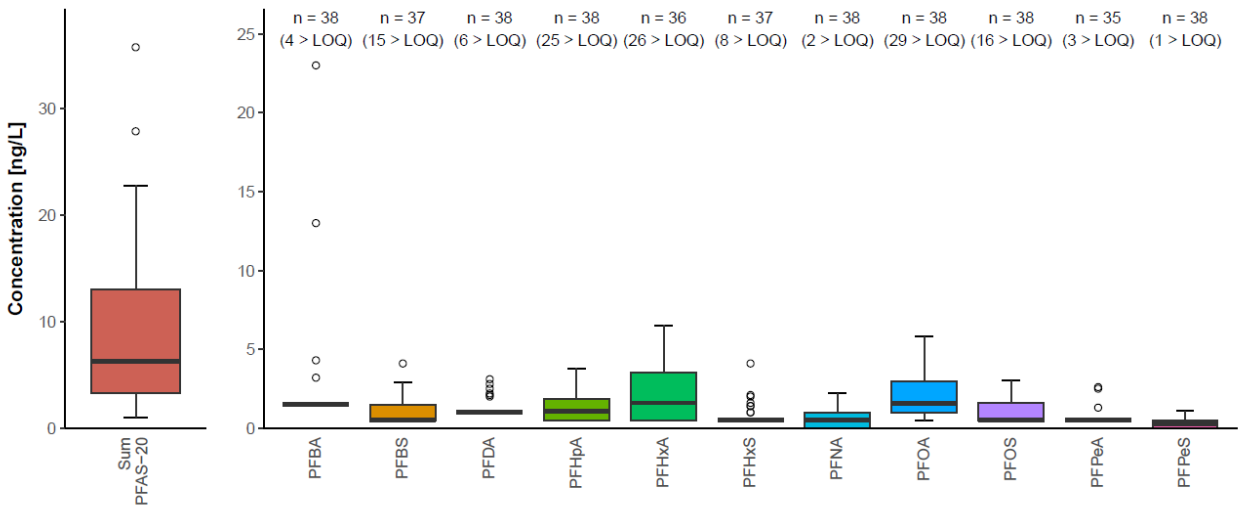

Figure 3. Concentrations for PFAS in stormwater runoff from two industrial catchments (n=38 storm events); horizontal bars – median values, boxes – 25 & 75% quantiles, whiskers – 10% & 90% quantiles, circles – values outside the 10%-90% range.

Results for individual PFAS compounds are shown in Figure 3. The compounds with the highest numbers of detections above the respective limits of quantification (LOQ) include PFOA (29), PFHxA (26), PFHpA (25), PFOS (16), and PFBS (15). The highest concentrations occurred for PFBA with a maximum of 23 ng/L. These concentrations are generally in a similar range compared to concentrations of PFAS in WWTP effluents as reported by Liu et al. (2023) for the upper Danube catchment. On the other hand, PFAS concentrations in stormwater runoff are higher compared to concentrations in rivers with low shares of WWTP effluents (<2%) as reported in the same study. This indicates that urban stormwater runoff from industrial sites can lead to increased PFAS concentrations in surface waters when discharged untreated.

Regarding the relevance of PFAS compounds as expressed by the risk potency factor (RPF) as referred to in the revision of the Water Framework Directive of the EU, PFNA (RPF=10), PFDA (RPF=7), PFOS (RPF=2) and PFOA (RPF=1) contribute the most to the total PFOA equivalent concentration (Figure 4). The boxplot for the sum of the PFOA equivalent concentrations for all samples is shown in Figure 4 (left) together with the proposed threshold value for surface waters of 4.4 ng/L (EC 2022). The median is just above the threshold value, indicating that more than half of the stormwater runoff samples exceeded the proposed thresholds for surface waters. The highest values are above 50 ng/L, resulting in an exceedance factor above ten. This shows the relevance of industrial stormwater runoff as source of PFAS for surface waters. However, as the thresholds will apply for surface waters and not for stormwater runoff itself, whether the thresholds might be exceeded depends on the dilution factor.

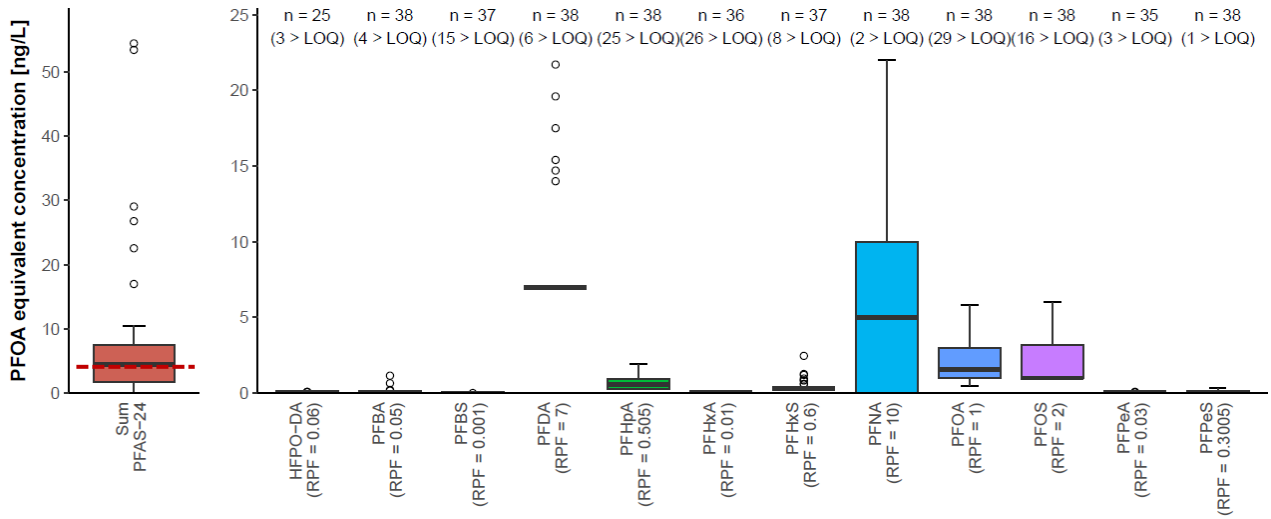

Figure 4. PFOA equivalent concentrations in stormwater runoff from two industrial catchments (n=38 storm events) determined using the risk potency factors (RPF) described in the revision of the EU Water Framework Directive. Left: sum of PFOA equivalent concentrations with proposed threshold value of 4.4 ng/L as red line, right: PFOA equivalent concentrations for individual PFAS compounds (indications of box, whisker, and circle values as in Figures 2 and 3).

Smaller urban streams that often receive high stormwater inputs (particularly in cities with separate sewer systems dominating the stormwater discharge pathways, as is the case in Berlin) and rivers with low flows are at particular risk.

Differences between sites

The concentrations of samples taken at the smaller industrial catchment MIR (with two pharmaceutical companies) were usually similar or lower for most of the analysed compounds compared to the larger catchment (GEW) with two main exceptions. Regarding PFAS, PFHxS was detected much more frequently and at higher concentrations at the MIR site compared to only one single detection at the GEW site (Figure 5). Additionally, the concentrations of benzotriazole were about twice as high at the MIR site (mean concentration: 0.33 µg/L) compared to the GEW site (mean concentration: 0.17 µg/L). An explanation could be the presence of metal metalworking industry or dry-cleaning facilities.

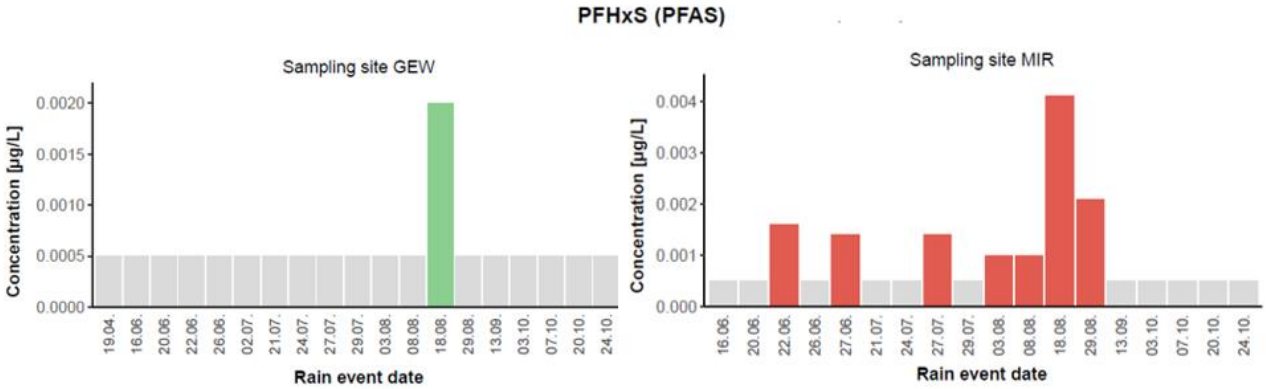

Figure 5. Concentrations of PFHxS in stormwater runoff of individual storm events from sample sites GEW (left) and MIR (right); grey bars indicate the limit of quantification.

Conclusions and future work

Stormwater runoff from two industrial catchments was successfully sampled over a period of 8 months to derive event mean concentrations of pollutants for individual storm events. Results show a variety of industrial, persistent, mobile and toxic substances (iPMTs) present in stormwater runoff, including 12 PFAS (out of 26), 13 pesticides (out of 39), all 16 PAHs and 8 industrial chemicals (4 organophosphates, 3 azoles and dioxane) which were analysed. Results further show that PFOA-equivalent concentrations for PFAS-24 exceeded the proposed revision of the EU Water Framework Directive for the majority of samples. It can be concluded that urban stormwater runoff from industrial sites can be a relevant source of PFAS in urban surface waters.

Future work includes comparison of the results to samples taken at an urban lake, which is not only the receiving surface water for the catchments investigated in this work, but is also potentially affected by PFAS contamination from a nearby legacy site affected by firefighting foams.

Acknowledgements

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